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Diphosphite ligands based on ribose backbone as suitable ligands in the hydrogenation and hydroformylation of prochiral olefins

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Abstract

Rh(I) and Ir(I) cationic complexes [M(cod)(PP)]BF_4 have been synthesised from diphosphite ligands **4–6** derived from ribofuranose. They have been used in the rhodium and iridium catalysed asymmetric hydrogenation of acrylic acid derivatives. Ribose derivative ligands **4–6** have also been used as auxiliaries in the Rh-catalysed hydroformylation of styrene. Hydroformylation results have been explained on the basis of the species formed under hydroformylation conditions. Comparative experiments with the related epimer D-(+)-xylose derivatives showed that the configuration of the product is controlled by the absolute configuration of the stereogenic carbon atom C-3.

1. Introduction

Ever since the early seventies there has been a great deal of interest in the asymmetric hydroformylation of several functionalised alkenes[1–3] whose chiral aldehydes can be used as starting material for the synthesis of fine chemicals.[4,5] Platinum–diphosphane complexes are highly enantioselective hydroformylation catalysts, but low chemo- and regioselectivity have been obtained.[6–8] During the last decade considerable attention has been devoted to phosphites as suitable ligands for hydroformylation catalysts.[9–14] One of the major advantages of phosphites is that they are easy to prepare and are not as sensitive to air as phosphanes.[15,16] Moreover they enable the selectivity of the hydroformylation reaction to be tuned to linear or branched products.[17–19] Excellent enantioselectivities have been recently obtained with Rh–diphosphite and Rh–phosphane–phosphite hydroformylation catalysts.[9–11]

The asymmetric hydrogenation of prochiral compounds catalysed by transition-metal complexes that contain chiral phosphorus ligands has been extensively used in organic synthesis[20–22] and some processes have found applications in industry.[23–25] Very little attention, however, has been paid to diphosphites as ligands in asymmetric hydrogenation.

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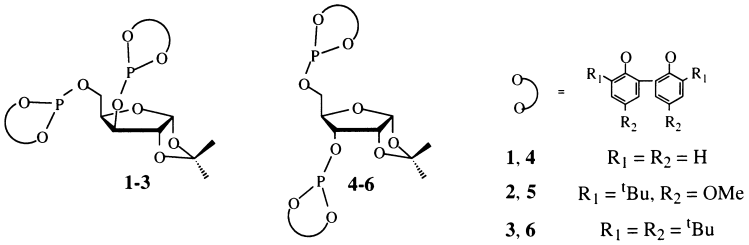
In recent studies, sugar derived ligands showed good conversions and excellent enantioselectivities in different types of catalytic reactions, e.g. hydrogenation,[26,27] hydrocyanation,[28] allylic alkylation,[29] which demonstrate their potential utility. However, the potential of the carbohydrate chiral pool for providing chiral diphosphites has hardly been exploited.[27,30–32] One of the most successful families of sugar diphosphites applied in hydroformylation is the 1,2-*O*-isopropylidene-α-xylofuranose derivatives **1**–**3** (Scheme 1).[31] These ligands have also shown good conversions and moderate enantioselectivities in the hydrogenation of acrylic acid derivatives.[33]

This paper discusses the results of the related and previously reported epimeric ribose derivatives[32] **4**–**6** in the asymmetric hydrogenation and hydroformylation of prochiral olefins. They provide further information about how the chirality of the sugar backbone is transferred to the products.

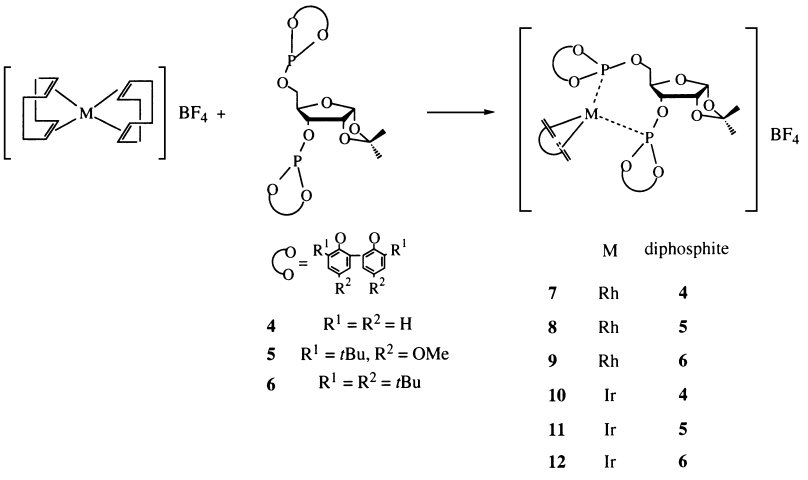


Scheme 1.

2. Results and discussion

2.1. Rhodium and iridium complexes

Carbohydrate diphosphites **4**–**6** react readily with $[M(cod)_2]BF_4$ (M = Rh, Ir) in dichloromethane, even with a large excess of diphosphite, to provide high yields of the corresponding $[M(cod)(PP)]^+$ cationic complexes (Scheme 2).



Scheme 2. Synthesis of complexes $[M(cod)(PP)]BF_4$ **7**–**12**

The ^{31}P NMR spectra of the rhodium complexes showed two signals split into clearly resolved double doublets due to the ^{31}P,^{103}Rh and ^{31}P,^{31}P couplings, except for complex **8**, which showed only one doublet because the chemical shifts of both phosphorus atoms accidentally coincide for a single isomer or for different species in fluxional behaviour on the NMR time-scale. The iridium complexes **10**–**12** showed two doublets due to the ^{31}P,^{31}P coupling. When the temperature was lowered, none of the rhodium or iridium complexes showed any splitting, which indicates that only one isomer is present, unlike the related xylofuranose derivatives, for which two isomers were observed.[33] In the case of complex **8**, it suggests also that the presence of only one doublet for the two phosphorus atoms is caused by an accidental isocronicity.

2.2. Hydrogenation of acrylic acid derivatives

Cationic complexes $[M(cod)(PP)]^+$ (M = Rh, Ir; PP = **4**–**6**) **7**–**12** have been used in the asymmetric hydrogenation of itaconic acid **13** and α-methyl(acetamido)acrylic ester **14** under mild conditions. Conversion and enantioselectivity results are shown in Table 1.

The $[Rh(cod)(PP)]^+$ **7**–**9** complexes gave better conversions in toluene/methanol than in CH_2Cl_2/methanol while the $[Ir(cod)(PP)]^+$ complexes **10**–**12** were more efficient in CH_2Cl_2/methanol, as previously observed for the related catalyst precursors that contain the epimer ligands **1**–**3**.[33]

The introduction of *tert*-butyl groups onto the *ortho* positions in the diphosphites produces an important effect on rate and enantioselectivity. In contrast with the results reported by Reetz and Neugebauer[27] conversions are higher for the precursors which contain the bulky and electron-rich ligands **2**–**3** (entries 3 and 5 versus 1; entries 8 and 10 versus 7). This is probably because they favour the oxidative addition reactions in the catalytic cycle.[33] The best enantioselectivities for the rhodium-catalysed hydrogenation of itaconic acid are obtained for precursor **7**, which contains the less hindered ligand **4** (entries 1 and 2).

Substrate **13** was hydrogenated with higher rates than substrate **14** for all catalytic precursors. For itaconic acid **13** the iridium complexes **11**–**12** were more active at 1 bar of H_2 than their rhodium counterparts. It is important to note that the sense of the enantioselectivity inductions obtained with iridium precursors **11** and **12** were opposite to those obtained with their rhodium counterparts **8** and **9**. For enamide **14** the enantiomeric excesses obtained with the iridium complexes were higher than those obtained with the rhodium catalysts.

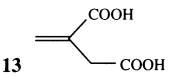
The catalytic precursors with ribose diphosphites **4**–**6** are generally less active and enantioselective than the related with the epimers derived from D-(+)-xylose **1**–**3**.[33] For itaconic acid the sense of the enantioselectivity was generally the same as with the catalytic precursors containing D-(+)-xylose-derivative ligands. However, for the acrylic ester derivative **14** the opposite direction was always obtained.

2.3. Hydroformylation of styrene and derivatives

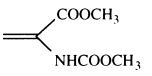
Diphosphites **4**–**6** have been used in the rhodium-catalysed asymmetric hydroformylation of styrene (Table 2). The catalysts were prepared in situ under typical hydroformylation conditions (40°C, 25 bar, 16 h) before the substrate was added.[34,35]

For all ligands regioselectivity for the branched aldehyde (88–98%) is good. As expected, the enantioselectivity varies according to the substitution of the ligand. Enantioselectivities were high with the catalyst containing ligands **5** and **6**, which have bulky *tert*-butyl substituents at the *ortho* positions of the bisphenol moieties (entries 2 and 3 versus 1).

Table 1
Hydrogenation of prochiral substrates with [M(cod)(PP)]BF_4 **7–12**, M = Rh, Ir



13



14

Entry	Precursor	Substrate	P (atm)	t (h)	% conv.	%ee
1	**7** [b]	**13**	5	6	31	50 (*R*)
2	**7** [b]	**13**	5	20	100	50 (*R*)
3	**8** [b]	**13**	5	6	62	11 (*R*)
4	**8** [b]	**13**	5	20	100	10 (*R*)
5	**9** [b]	**13**	5	6	57	11 (*R*)
6	**9** [b]	**13**	5	20	100	11 (*R*)
7	**10** [c]	**13**	5	20	47	8 (*R*)
8	**11** [c]	**13**	1	2	88	14 (*S*)
9	**11** [c]	**13**	1	6	100	13 (*S*)
10	**12** [c]	**13**	1	2	83	15 (*S*)
11	**12** [c]	**13**	1	6	100	15 (*S*)
12	**12** [c]	**14**	1	20	30	37 (*R*)
13	**11** [c]	**14**	1	20	24	28 (*R*)
14	**9** [b]	**14**	5	20	56	4 (*R*)
15	**8** [b]	**14**	5	20	88	6 (*R*)

[a] Conditions: [cat]/[itaconic acid] = 1/100. Itaconic acid = 2 mmol. Solvent = 12 ml. T = 313 K
[b] Toluene / methanol (2 / 1). [c] CH_2Cl_2 / methanol (2 / 1).

Replacement of *tert*-butyl by methoxy substituent at the *para* positions of the present bisphenol moiety produces somewhat higher enantioselectivities (entry 2 versus 3).

The highest enantiomeric excess (up to 61%) was achieved using ligand **5** at 25°C but the reaction rate turned to an impractically low value (entry 4).

For comparison purposes, hydroformylation experiments under the same conditions were carried out with the previously reported xylose diphosphites.[31] Ligands based on 1,2-*O*-isopropylidene-xylofuranose containing a *tert*-butyl group in *ortho* positions gave (*S*)-aldehydes, while ligands with ribofuranose backbone gave (*R*)-aldehydes with similar enantioselectivities (entries 6 and 7 versus 2 and 3). These opposite asymmetric inductions and the similar conversions and regioselectivities suggest that the absolute configuration at the stereogenic carbon atom

Table 2
Hydroformylation results[a]

Entry	Ligand	Substrate	TOF[b]	%conv[c]	%2PP[d]	%ee[e]
1	**4**	Styrene	44	19	88	25 (*S*)
2	**5**	Styrene	41	19	96	53 (*R*)
3	**6**	Styrene	55	26	98	45 (*R*)
4[f]	**5**	Styrene	5	3(17)[g]	97	61 (*R*)
5	**1**	Styrene	40	17	84	4 (*S*)
6	**2**	Styrene	50	20	95	51 (*S*)
7	**3**	Styrene	53	20	95	41 (*S*)
8	**2**	p-F-Styrene	54	23	95	51 (*S*)
9	**2**	p-OMe-Styrene	53	26	94	51 (*S*)

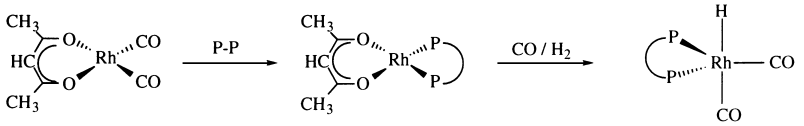
[a] Substrate/Rh molar ratio is 1000, P= 25 bar, toluene= 15 mL, T = 40°C, P_{CO}/P_{H2} = 1. [b] TOF in mol aldehyde x mol Rh^{-1} x h^{-1} measured at 1 h. [c] % Conversion of styrene after 5h. [d] % in 2-phenylpropanal. [f] T = 25°C. [g] Conversion measured after 3 days.

C-3 produces an overall opposite absolute structure of the hydroformylation catalysts and hereby induces opposite enantioselectivities.

Introduces different groups in *para* position in the substrate does not seem to affect the conversion, regioselectivitity or enantioselectivity of the hydroformylation (entries 6, 8 and 9).

2.4. Characterisation of [HRh(PP)(CO)$_2$] complexes

Hydrido rhodium diphosphite dicarbonyl complexes, which are generally considered to be active catalysts,[9–14] were prepared from a starting rhodium precursor such as [Rh(acac)(CO)$_2$] by adding 1 equivalent of diphosphite under hydroformylation conditions (Scheme 3).



15 P-P = **4**

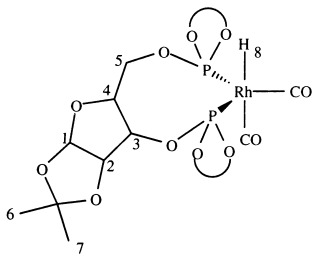
16 P-P = **5**

17 P-P = **6**

Scheme 3. Synthesis of complexes [HRh(PP)(CO)$_2$] **15**–**17**

The solution structures of hydridorhodium diphosphite dicarbonyl catalysts [HRh(PP)(CO)$_2$], PP = diphosphite ligand, were studied by ^{1}H and ^{31}P HP NMR spectroscopy.[11,31,34] Table 3

Table 3
Selected ^{1}H and ^{31}P NMR data for hydrido-carbonyl rhodium complexes **16** and **17**



	16		**17**	
Position	δ (ppm)	*J* (Hz)	δ (ppm)	*J* (Hz)
1	5.72 (d)	$^{3}J_{1\text{-}2} = 3.6$	5.79 (d)	$^{3}J_{1\text{-}2} = 3.6$
2	4.81 (dd)	$^{3}J_{2\text{-}3} = 4.2$	4.79 (dd)	$^{3}J_{2\text{-}3} = 4.1$
3	4.39 (m)		4.45 (m)	
4	4.11 (m)		4.22 (m)	
5	3.45 (m)		4.05 (m)	
5'	3.10(m)		4.05 (m)	
6	1.14 (s)		1.14 (s)	
7	1.42 (s)		1.51 (s)	
8	-10.3 (br)		-10.4 (br)	
P	161.9 (dd)	$^{2}J_{P\text{-}P} = 312$	162.4 (dd)	$^{2}J_{P\text{-}P} = 308$
		$^{1}J_{P\text{-}Rh} = 266$		$^{1}J_{P\text{-}Rh} = 264$
P	165.7 (dd)	$^{1}J_{P\text{-}Rh} = 273$	166.1 (dd)	$^{1}J_{P\text{-}Rh} = 259$

shows the selected data obtained for complexes **16** and **17**. Fairly long reaction times (4–8 h) at 25 bar syngas were needed for the complete formation of $[HRh(PP)(CO)_2]$. Shorter reaction times revealed the formation of intermediate species as side products in the ^{31}P NMR spectra with phosphorus–rhodium coupling constants around 300 Hz.[11]

At 298 K the ^{31}P HP NMR spectra for hydrido dicarbonyl complexes **16** and **17** showed a broad eight-line spectrum ($\Delta\omega_{1/2}$ around 30 Hz) due to the ^{31}P,^{31}P and ^{31}P,^{103}Rh couplings (ABX system). The same broad NMR pattern is observed at low temperature (298–203 K). These suggest fluxional processes on the NMR time scale. This was confirmed by measuring the ^{31}P NMR spectra at 333 K which showed sharp signals ($\Delta\omega_{1/2}$ around 10 Hz) (Fig. 1). The large values for the $^{1}J_{P-Rh}$ are characteristic of phosphite ligands coordinated in an equatorial position.[11,31]

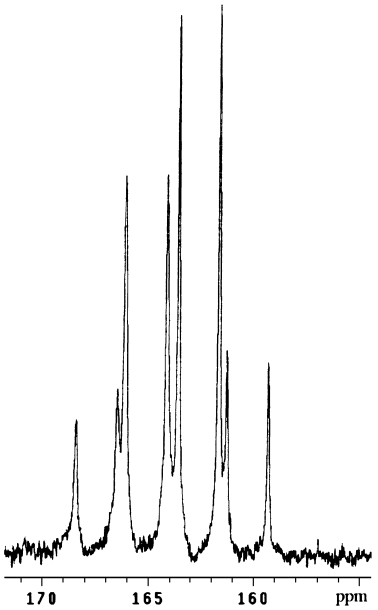


Figure 1. $^{31}P\{^{1}H\}$ HP NMR spectrum of compound **16** at 333 K

The ^{1}H NMR spectra in the hydride region revealed a broad signal between 333 and 203 K for complexes **16** and **17**, due to the small coupling constants of hydrogen with rhodium and with the two phosphorus atoms.

The ^{31}P and ^{1}H NMR data are consistent with the presence of two diastereoisomers, whose diphosphites coordinate bisequatorially to the rhodium in a fast exchange on the NMR time scale.

Complex **15** containing ligand **4** showed several catalytic hydride rhodium species in different proportions. This is due to the presence of different atropoisomers of the bisphenol moiety in the diphosphite ligand. The ambient temperature ^{31}P NMR spectrum for the major diastereoisomer showed the expected eight-line spectrum for an ABX system. The simulation of these signals affords the two phosphorus atoms located at 169.2 ($^{2}J_{P-P} = 324$ Hz, $^{1}J_{P-Rh} = 278$ Hz) and 172.3 ppm ($^{1}J_{P-Rh} = 261$ Hz). The ^{1}H NMR for this isomer in the hydride region revealed a double triplet at -9.9 ppm ($^{1}J_{Rh-H} = 5.4$ Hz, $^{2}J_{P-H} = 32.4$ Hz), not the expected double double doublet, because the coupling constants with the two non-equivalent phosphorus atoms located in equatorial position coincide. The relatively large phosphorus–hydride coupling constant is indicative of a distorted trigonal bipyramidal hydride complex.[31]

3. Experimental

3.1. General comments

All syntheses were performed by standard Schlenk techniques under a nitrogen or argon atmosphere. The complexes $[Rh(cod)_2]BF_4$[36] and $[Ir(cod)_2]BF_4$[36] and the diphosphites **1**–**3**[31] and **4**–**6**[32] were prepared by previously described methods. Solvents were purified by standard procedures. All other reagents were used as commercially available. Elemental analyses were performed on a

Perkin–Elmer 240 B instrument. ^{1}H, $^{13}C\{^{1}H\}$ and $^{31}P\{^{1}H\}$ NMR spectra were recorded on a Variant Gemini 300 MHz spectrometer. Chemical shifts are relative to $SiMe_4$ (^{1}H and ^{13}C) as internal standard or H_3PO_4 (^{31}P) as external standard. All assignments in NMR spectra were determined by means of COSY and HETCOR spectra. EI Mass spectra were obtained on a HP 5989 A spectrometer. VG-Autospect equipment was used for FAB mass spectral analyses. The matrix was *m*-nitrobenzylalcohol. Gas chromatographic analyses were run on a Hewlett–Packard HP 5890A instrument (split/splitless injector, J&W Scientific, Ultra-2 25 m column, internal diameter 0.2 mm, film thickness 0.33 mm, carrier gas: 150 kPa He, F.I.D. detector) equipped with a Hewlett–Packard HP 3396 series II integrator. Hydroformylation reactions were carried out in a home-made 100 mL stainless steel autoclave. Enantiomeric excesses were measured after oxidation of the aldehydes to the corresponding carboxylic acids on a Hewlett–Packard HP 5890A gas chromatograph (split/splitless injector, J&W Scientific, FS-Cyclodex β-I/P 50 m column, internal diameter 0.2 mm, film thickness 0.33 mm, carrier gas: 100 kPa He, F.I.D. detector). Absolute configuration was determined by comparing the retention times with enantiomerically pure (*S*)-2-phenylpropionic and *R*-2-phenylpropionic acid derivatives. Hydrogenations at 5 bar were carried out in a home-made 100 mL stainless steel autoclave. The reaction under 1 atm of H_2 was performed in a previously described hydrogen–vacuum line.[37] The enantiomeric excesses for the methylsuccinic acid were determined by polarimetry,[38] while for *N*-acetylalanine methyl ester they were determined by gas chromatography using an L-Chirasil-Val column.

3.2. Preparation of cationic complexes

3.2.1. General procedure

Diphosphite ligand (0.1 mmol) was added to a solution of $[M(cod)_2](BF_4)$ (0.1 mmol; M = Rh, 40.5 mg; M = Ir, 49.4 mg) in 2 mL of dichloromethane. After 10 min, the desired products were obtained by precipitation with hexane.

*3.2.1.1. [Rh(cod)(**4**)]BF_4 7*. 81 mg (89%, yellow solid). Elemental analysis. Found (%): C, 52.05; H, 4.48. Calculated (%) for $C_{40}H_{40}BF_4O_9P_2Rh$: C, 52.42; H, 4.40. FAB spectrometry: m/z: 829 [M^+]. ^{31}P NMR ($CDCl_3$), δ (ppm): 137.64 (dd, 1P, $^{2}J_{P-P}$ = 49.5 Hz, $^{1}J_{P-Rh}$ = 253.9 Hz), 137.77 (dd, 1P, $^{2}J_{P-P}$ = 49.5 Hz, $^{1}J_{P-Rh}$ = 251.9 Hz). ^{1}H NMR ($CDCl_3$), δ (ppm): 1.31 (s, 3H, CH_3), 1.41 (s, 3H, CH_3), 1.82 (m, 2H, CH_2), 1.98 (m, 2H, CH_2), 2.44 (m, 2H, CH_2), 2.84 (m, 2H, CH_2), 4.31 (m, 1H, H-4), 4.48 (m, 1H, H-5′), 4.90 (m, 1H, H-5), 5.05 (dd, 1H, H-2, $^{3}J_{2-1}$ = 3.0 Hz, $^{3}J_{2-3}$ = 3.6 Hz), 5.32 (m, 1H, CH=), 5.51 (M, 1H, CH=), 5.68 (m, 1H, H-3), 6.03 (d, 1H, H-1, $^{3}J_{1-2}$ = 3.0 Hz), 6.21 (m, 2H, CH=), 7.2–7.6 (m, 16H, arom.). ^{13}C NMR ($CDCl_3$), δ (ppm): 26.3 (CH_3), 26.6 (CH_3), 29.3 (CH_2), 30.5 (CH_2), 30.6 (CH_2), 67.5 (C-5), 74.6 (t, C-4, J_{P-C} = 3.8 Hz), 78.8 (t, C-3, J_{P-C} = 4.0 Hz), 79.2 (d, C-2, J_{P-C} = 2.3 Hz), 104.2 (C-1), 107.6 (m, CH=), 109.4 (m, CH=), 111.4 (m, CH=), 112.0 (m, CH=), 113.6 (CMe_2), 121.3, 122.0, 122.1, 125.9, 126.7, 127.1, 127.2 (CH=), 128.8 (C), 129.7 (CH=), 129.8 (C), 129.9 (CH=), 130.0 (C), 130.2, 130.4, 130.7, 130.9 (CH=).

*3.2.1.2. [Rh(cod)(**5**)]BF_4 **8***. 105 mg (87%, yellow solid). Elemental analysis. Found (%): C, 55.98; H, 6.36. Calculated (%) for $C_{60}H_{80}BF_4O_{13}P_2Rh{\cdot}1/2CH_2Cl_2$: C, 55.75; H, 6.27. FAB spectrometry: m/z: 1175 [M^+]. ^{31}P NMR ($CDCl_3$), δ (ppm): 123.8 (d, $^{1}J_{Rh-P}$ = 255 Hz). ^{1}H NMR ($CDCl_3$), δ (ppm): 1.20 (s, 3H, CH_3), 1.35 (s, 3H, CH_3), 1.47 (s, 18H, CH_3 ^{t}Bu), 1.68 (s, 9H, CH_3 ^{t}Bu), 1.70 (s, 9H, CH_3 ^{t}Bu), 1.92 (m, 2H, CH_2), 2.19 (m, 2H, CH_2), 2.28 (m, 2H, CH_2), 2.32 (m,

2H, CH_2), 3.27 (dd, 1H, H-2, $^3J_{2-1}=3.3$ Hz, $^3J_{2-3}=3.0$ Hz), 3.49 (m, 1H, H-5′), 3.81 (s, 12H, OMe), 3.92 (m, 1H, H-5), 4.42 (m, 2H, H-3, H-4), 5.18 (m, 1H, CH=), 5.41 (m, 1H, CH=), 5.43 (d, 1H, H-1, $^3J_{1-2}=3.3$ Hz), 6.20 (m, 1H, CH=), 6.29 (m, 1H, CH=), 6.60 (m, 2H, CH=, arom), 6.69 (m, 1H, CH=, arom.), 6.74 (m, 1H, CH=, arom.), 7.04 (m, 4H, CH=, arom.). ^{13}C NMR ($CDCl_3$), δ (ppm): 25.5 (CH_3), 26.3 (CH_3), 27.7 (CH_2), 28.5 (CH_2), 32.0 (CH_3, ^{t}Bu), 32.1 (CH_3, ^{t}Bu), 32.2 (CH_3, ^{t}Bu), 35.3 (C, ^{t}Bu), 35.4 (C, ^{t}Bu), 35.6 (C, ^{t}Bu), 55.7 (OCH_3), 69.8 (dd, C-5, $J_{P-C}=9.7$ Hz, $J_{P-C}=3.5$ Hz), 71.2 (t, C-4, $J_{P-C}=4.0$ Hz), 77.0 (C-2), 77.3 (dd, C-3, $J_{P-C}=5.1$ Hz, $J_{P-C}=2.8$ Hz), 101.5 (m, CH=), 102.8 (m, CH=), 103.1 (C-1), 109.7 (m, CH=), 112.9 (CH=), 113.2 (CMe_2), 113.7, 114.3, 114.7, 115.5, 115.9 (CH=), 128.0, 131.3, 131.9 (C), 132.4 (CH=), 141.9, 142.3, 142.9, 156.5, 156.7, 157.3 (C).

*3.2.1.3. [Rh(cod)(**6**)]BF_4 **9**.* 120 mg (88%, yellow solid). Elemental analysis. Found (%): C, 62.36; H, 7.57. Calculated (%) for $C_{72}H_{104}BF_4O_9P_2Rh\cdot 1/2CH_2Cl_2$: C, 61.91; H, 7.52. FAB spectrometry: m/z: 1277 [M^+]. ^{31}P NMR ($CDCl_3$), δ (ppm): 122.7 (dd, 1P, $^2J_{P-P}=26.7$ Hz, $^1J_{P-Rh}=266.6$ Hz), 123.6 (dd, 1P, $^2J_{P-P}=26.7$ Hz, $^1J_{P-Rh}=265.3$ Hz). ^{1}H NMR ($CDCl_3$), δ (ppm): 1.11 (s, 3H, CH_3), 1.37 (m, 39H, CH_3, CH_3 ^{t}Bu), 1.48 (m, 18H, CH_3 ^{t}Bu), 1.62 (m, 18H, CH_3 ^{t}Bu), 1.81 (m, 2H, CH_2), 2.20 (m, 2H, CH_2), 2.45 (m, 2H, CH_2), 2.62 (m, 2H, CH_2), 3.21 (dd, 1H, H-2, $^3J_{2-1}=2.7$ Hz, $^3J_{2-3}=2.4$ Hz), 3.48 (m, 1H, H-5′), 3.92 (m, 1H, H-5), 4.44 (m, 2H, H-3, H-4), 5.15 (m, 1H, CH=), 5.37 (d, 1H, H-1, $^3J_{1-2}=2.7$ Hz), 5.44 (m, 1H, CH=), 6.18 (m, 1H, CH=), 6.31 (m, 1H, CH=), 7.17 (m, 2H, CH=), 7.21 (m, 2H, CH=), 7.52 (m, 4H, CH=). ^{13}C NMR ($CDCl_3$), δ (ppm): 26.3 (CH_3), 26.4 (CH_3), 27.7 (CH_2), 28.7 (CH_2), 31.2 (CH_3, ^{t}Bu), 31.3 (CH_3, ^{t}Bu), 31.6 (CH_3, ^{t}Bu), 32.3 (CH_3, ^{t}Bu), 32.4 (CH_3, ^{t}Bu), 34.6 (C, ^{t}Bu), 35.3 (C, ^{t}Bu), 35.4 (C, ^{t}Bu), 69.3 (d, C-5, $J_{P-C}=14.8$ Hz), 70.9 (d, C-3, $J_{P-C}=6.2$ Hz), 77.2 (d, C-2, $J_{P-C}=3.4$ Hz), 77.4 (m, C-4), 101.8 (m, CH=), 102.7 (C-1), 103.2 (m, CH=), 109.9 (m, CH=), 113.4 (CMe_2), 124.8, 125.2, 125.4, 126.2, 127.4, 128.0, 128.5 (CH=), 130.2 (C), 130.8 (CH=), 131.3, 139.9, 140.5, 148.5, 148.9, 149.5 (C).

*3.2.1.4. [Ir(cod)(**4**)]BF_4 **10**.* 82 mg (83%, white solid). Elemental analysis. Found (%): C, 47.77; H, 4.12. Calculated (%) for $C_{40}H_{40}BF_4IrO_9P_2$: C, 47.82; H, 4.32. FAB spectrometry: m/z: 919 [M^+]. ^{31}P NMR ($CDCl_3$), δ (ppm): 104.8 (s). ^{31}P NMR ($CDCl_3$, 233 K), δ (ppm): 103.1 (d, $^2J_{P-P}=54$ Hz), 105.9 (d, $^2J_{P-P}=54$ Hz). ^{1}H NMR ($CDCl_3$), δ (ppm): 1.24 (s, 3H, CH_3), 1.41 (s, 3H, CH_3), 1.80–2.80 (m, 8H, CH_2), 3.80–4.70 (m, 5H, H-2, H-3, H-5, H-5′), 5.31 (m, 2H, CH=), 5.52 (d, 1H, H-1, $^3J_{1-2}=3.9$ Hz), 5.57 (m, 2H, CH=), 6.80–7.80 (m, 16H, CH=).

*3.2.1.5. [Ir(cod)(**5**)]BF_4 **11**.* 109 mg (87%, red solid). Elemental analysis. Found (%): C, 54.58; H, 6.56. Calculated (%) for $C_{60}H_{80}BF_4IrO_{13}P_2\cdot 1/2CH_2Cl_2$: C, 54.36; H, 6.71. FAB spectrometry: m/z: 1263 [M^+]. ^{31}P NMR ($CDCl_3$), δ (ppm): 113.6 (d, 1P, $^2J_{P-P}=43.1$ Hz), 114.9 (d, 1P, $^2J_{P-P}=43.1$ Hz). ^{1}H NMR ($CDCl_3$), δ (ppm): 1.25 (s, 3H, CH_3), 1.40 (s, 3H, CH_3), 1.54 (s, 18H, CH_3 ^{t}Bu), 1.64 (s, 18H, CH_3 ^{t}Bu), 2.05 (m, 4H, CH_2), 2.30 (m, 2H, CH_2), 2.56 (m, 2H, CH_2), 3.22 (dd, 1H, H-2, $^3J_{2-1}=3.3$ Hz, $^3J_{2-3}=3.6$ Hz), 3.59 (m, 1H, H-5′), 3.82 (s, 12H, OMe), 4.00 (m, 1H, H-5), 4.45 (m, 2H, H-3, H-4), 4.84 (m, 1H, CH=), 5.08 (m, 1H, CH=), 5.40 (d, 1H, H-1, $^3J_{1-2}=3.3$ Hz), 6.03 (m, 1H, CH=), 6.14 (m, 1H, CH=), 6.65 (m, 2H, CH=), 6.77 (m, 2H, CH=), 7.05 (m, 4H, CH=). ^{13}C NMR ($CDCl_3$), δ (ppm): 25.9 (CH_3), 26.7 (CH_3), 28.4 (CH_2), 29.3 (CH_2), 31.0 (CH_2), 31.9 (CH_3, ^{t}Bu), 32.3 (CH_3, ^{t}Bu), 32.6 (CH_3, ^{t}Bu), 32.9 (CH_3, ^{t}Bu), 35.9 (C, ^{t}Bu), 36.0 (C, ^{t}Bu), 56.2 (OCH_3), 70.6 (d, C-5, $J_{P-C}=14.3$ Hz), 71.8 (d, C-3, $J_{P-C}=6.8$ Hz), 77.6 (C-2), 78.2 (d, C-4, $J_{P-C}=13.7$ Hz), 92.3 (d, CH=, $J_{C-P}=16.6$ Hz), 93.7 (d, CH=, $J_{C-P}=16.5$ Hz), 101.4

(d, CH=, J_{C-P} = 13.2 Hz), 101.7 (d, CH=, J_{C-P} = 13.2 Hz), 103.7 (C-1), 113.6 (CH=), 113.9 (CMe_2), 114.7, 115.1, 115.4, 115.5, 115.9, 116.5 (CH=), 129.2, 131.8, 132.4, 132.5, 132.9, 142.6, 142.7, 142.9, 157.0, 157.3, 157.8, 157.9 (C).

*3.2.1.6. [Ir(cod)(**6**)]BF_4 **12***. 140 mg (89%, red solid). Elemental analysis. Found (%): C, 59.54; H, 7.45. Calculated (%) for $C_{72}H_{104}BF_4IrO_9P_2$: C, 59.45; H, 7.21. FAB spectrometry: m/z: 1365 [M^+]. ^{31}P NMR ($CDCl_3$), δ (ppm): 112.7 (d, 1P, $^2J_{P-P}$ = 43.1 Hz), 113.3 (d, 1P, $^2J_{P-P}$ = 43.1 Hz). ^{1}H NMR ($CDCl_3$), δ (ppm): 1.24 (s, 18H, CH_3 ^{t}Bu), 1.32 (s, 3H, CH_3), 1.47 (m, 3H, CH_3), 1.56 (m, 18H, CH_3 ^{t}Bu), 1.78 (m, 18H, CH_3 ^{t}Bu), 1.90 (m, 18H, CH_3 ^{t}Bu), 2.02 (m, 4H, CH_2), 2.37 (m, 4H, CH_2), 3.04 (dd, 1H, H-2, $^3J_{2-1}$ = 3.3 Hz, $^3J_{2-3}$ = 3.1 Hz), 3.50 (m, 1H, H-5′), 3.87 (m, 1H, H-5), 4.39 (m, 2H, H-3, H-4), 4.72 (m, 1H, CH=), 5.01 (m, 1H, CH=), 5.24 (d, 1H, H-1, $^3J_{1-2}$ = 3.3 Hz), 5.88 (m, 1H, CH=), 6.02 (m, 1H, CH=), 7.04 (m, 2H, CH=), 7.15 (m, 2H, CH=), 7.46 (m, 4H, CH=). ^{13}C NMR ($CDCl_3$), δ (ppm): 26.9 (CH_3), 29.5 (CH_2), 29.7 (CH_2), 31.0 (CH_2), 31.7 (CH_3, ^{t}Bu), 32.2 (CH_3, ^{t}Bu), 32.6 (CH_3, CH_2), 32.7 (CH_3, ^{t}Bu), 32.8 (CH_3, ^{t}Bu), 33.1 (CH_3, ^{t}Bu), 35.1 (C, ^{t}Bu), 35.2 (C, ^{t}Bu), 35.9 (C, ^{t}Bu), 36.0 (C, ^{t}Bu), 70.2 (dd, C-5, J_{P-C} = 12.6 Hz, J_{P-C} = 1.8 Hz), 71.6 (dd, C-3, J_{P-C} = 5.7 Hz, J_{P-C} = 2.9 Hz), 77.8 (d, C-2, J_{P-C} = 3.4 Hz), 78.3 (dd, C-4, J_{P-C} = 11.4 Hz, J_{P-C} = 2.9 Hz), 92.5 (dd, CH=, J_{P-C} = 13.7 Hz, J_{P-C} = 2.3 Hz), 93.9 (dd, CH=, J_{P-C} = 13.7 Hz, J_{P-C} = 2.1 Hz), 101.2 (d, CH=, J_{P-C} = 6.3 Hz), 101.4 (d, CH=, J_{P-C} = 5.7), 103.5 (C-1), 114.1 (CMe_2), 125.5, 125.9, 126.1, 126.9, 128.1, 128.2, 128.6, 129.1 (CH=), 130.8 (C), 131.5 (CH=), 131.7, 131.8, 140.5, 140.7, 141.2, 149.1, 149.5, 149.7, 150.2 (C).

3.3. Hydroformylation of styrene

The autoclave was purged three times with CO. The solution was formed from [Rh(acac)$(CO)_2$] (0.013 mmol) and diphosphite (0.017 mmol) in toluene (10 mL). After pressurising to the desired pressure with syngas and heating the autoclave to the reaction temperature, the reaction mixture was stirred for 15 h to form the active catalyst. The autoclave was depressurised and a solution of substrate (13 mmol) in toluene (5 mL) was brought into the autoclave and pressurised again. During the reaction several samples were taken from the autoclave. After the desired reaction time, the autoclave was cooled to room temperature and depressurised. The reaction mixture was analysed by gas chromatography. The aldehydes obtained from the hydroformylation were oxidised to carboxylic acids to determine the enantiomeric excess.

3.4. In situ HP NMR characterisation of [HRh(CO)$_2$(PP)]

In a typical experiment a sapphire tube (ϕ = 10 mm) was filled under argon with a solution of [Rh(acac)$(CO)_2$] (0.030 mmol) and ligand (molar ratio PRh = 1.1) in toluene-d_8 (1.5 mL). The HP NMR tube was purged twice with CO and pressurised to the appropriate pressure of CO/H_2. After a reaction time of 16 h shaking at the desired temperature, the solution was analysed.

3.5. Hydrogenation experiments

The reactions were performed in a home-made autoclave. The autoclave was purged three times with H_2. In a typical run, catalytic precursor (0.02 mmol) and substrate (2 mmol) were dissolved in the appropriate mixture of solvents (12 mL) and introduced in the purged autoclave. After pressurising to the desired pressure with hydrogen and heating the autoclave to the reaction

temperature, the reaction mixture was stirred. After the desired reaction time, the autoclave was cooled to room temperature and depressurised. The solvent was evaporated.

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